

Some Elementary Theoretical Considerations Concerning Superconductivity of Superimposed Metallic Films*

Abstract: A microscopic theory of superconductivity of superimposed metallic films is proposed, based on the fact that the electron pair correlation function penetrates into a normal metal where the electron-electron interaction would not by itself produce a superconducting state.

Smith, Shapiro, Miles and Nicol¹ have confirmed earlier reports by Meissner² and others of a change in the superconducting properties of thin metallic films in contact with thin films of other metals. Parmenter³ has constructed a theory of such contacts, but a boundary condition he employs is yet to be justified from more fundamental considerations. In this note we should like to present a simple microscopic theory of superconductivity in such contact neighborhoods based on a modification of the parameter $N(0)V$ which occurs in the BCS⁴ expression for the energy gap:

$$\epsilon_0 = 2(\hbar\omega)_{av} \exp[-1/N(0)V] \quad (1)$$

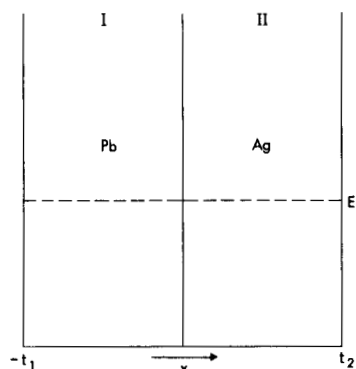
If two metallic samples—one a superconductor, the other not—are placed in contact, the properties of the entire material change from that of a superconductor in one material to that of a normal metal in the other. The range of the interaction between electrons that produces the superconducting state—the interaction due to phonon exchange and that due to the screened Coulomb repulsion—has been estimated to be about 10^{-8} cm.⁵ This might suggest that at a contact surface the change from superconducting to normal properties would occur in this very short distance. Because of the large coherence distance between zero momentum pairs, however, the superconducting correlation can extend deeply into a volume where the interaction between the electrons is in fact zero. In this respect the situation is similar to that of the deuteron whose wave function extends large distances beyond the range of the nuclear potential. This creates the possibility that thin films of differing metals deposited on one another can profoundly influence each other's superconducting properties.

For such superimposed films the electron-electron

interaction is a function not only of momenta and the relative coordinate of the two electrons, but also of the absolute position of the two electrons. Because of this interaction there is a non-zero matrix element $V_{\kappa'\kappa}$ for scattering from a two-electron state labelled by κ to one labelled by κ' . This matrix element summed over all κ' and averaged over κ in the interaction region yields $[N(0)V_{av}]$ in (1), which determines the energy gap and the transition temperature.

The essential observation made here is that this average will be decreased if the electron normalization volume is increased while the electron-electron interaction acts over only a part of the volume. This should result in a decrease of the transition temperature of a superconductor in contact with a normal metal. At the same time, under the proper circumstances, the same argument implies that *a normal film in contact with a superconductor can itself become a superconductor.*

To treat this problem precisely, one must construct a generalization of the BCS theory which can handle potentials that are not translationally invariant. This can be done conveniently using Green's function methods.⁶ The solution of the resulting equations in situations appropriate to superimposed films is being studied at present by W. Silvert of Brown University.



* Work supported in part by the U.S. Atomic Energy Commission.

† Alfred P. Sloan Research Fellow, Brown University, Providence, R.I.

To illustrate the physical effect we compute $[N(0)V]_{av}$ in the extremely simple case of two metals in perfect contact (no oxide barrier between them) with the same Fermi energy and the same effective mass. The films are in contact over the plane $x = 0$. The left-hand film (called I) has a thickness t_1 , while the right-hand film (called II) has a thickness t_2 . To further simplify we allow the electron-electron potential to have the form

$$V(r_1 r_2 \cdots) = -V\delta(r_1 - r_2) \quad x_1 \text{ and } x_2 \in I \\ = 0 \quad \text{otherwise.} \quad (2)$$

The wave function for an electron pair with the quantum numbers κ can be written

$$\psi_\kappa(r) = \frac{1}{t_1 + t_2} \chi_\kappa(r), \quad (3)$$

where

$$\chi_\kappa(r) = \frac{N}{\sqrt{2}} (e^{i\kappa \cdot r} + e^{-i\kappa \cdot r}), \quad (4)$$

is a properly symmetrized pair function; the extra constant N normalizes χ in the integration over the area of the film; $\hbar\kappa$ is the relative momentum of the pair, and $r = r_1 - r_2$ is the relative coordinate. The density of single electron states of one spin per unit energy at the Fermi surface is

$$N(0) = (t_1 + t_2)\eta(0), \quad (5)$$

where $\eta(0)$ is independent of t_1 or t_2 .

The scattering matrix element $V_{\kappa'\kappa}$ is then given by

$$V_{\kappa'\kappa} = \iint dr_1 dr_2 \psi_{\kappa'}^*(r_1 r_2) V(r_1 r_2) \psi_\kappa(r_1 r_2), \quad (6)$$

which for the potential (2) becomes

$$V_{\kappa'\kappa} = (-2V) \frac{t_1}{(t_1 + t_2)^2}. \quad (7)$$

This multiplied by the density of states (5) and properly averaged yields

$$[N(0)V]_{I+II} = \frac{t_1}{t_1 + t_2} [N(0)V]_I, \quad (8)$$

where $[N(0)V]_I$ is the interaction constant for a pure specimen of metal I while $[N(0)V]_{I+II}$ is that for films I and II in contact. Because of the exponential dependence of the energy gap on $N(0)V$, under the above conditions even the thinnest films of normal material would produce drastic alterations of the energy gap in a thin superconducting film.

Even for this average, however, matters are not this simple. The differing Fermi momenta in two metals produce refraction and, for some angles of incidence, total internal reflection. More important, under usual experimental conditions a chemisorbed oxygen layer is almost certain to form between the two metals. This will create a potential barrier of the order of several tenths of an electron volt for a distance of several

angstroms. Such a barrier will tend to separate the two materials, as will any mechanical barrier or separation.

We therefore expect that the factor $t_1/(t_1 + t_2)$ is an upper bound on the reduction of the effective interaction and that the actual reduction factor should have the form crudely

$$t_1/(t_1 + \beta t_2), \quad (9)$$

where $0 \leq \beta \leq 1$ and where β is determined by the barrier between films, the difference in effective mass and well depth—all of the effects which prevent electrons from freely moving from one film to the other. Preliminary calculations indicated that a reasonable value of β will crudely reproduce the data of Smith et al.¹

The arguments presented above have as a necessary converse the implication that the contact region of nonsuperconducting materials should become superconducting when in contact with superconductors. The effective penetration of electrons from one region to another is limited among other things by the electron mean free path; the further superconducting electrons penetrate into the "normal area" the smaller the energy gap should be. However, as there should be only one transition temperature for an entire sample, one might expect in a lead-silver contact that the energy gap would vary spatially, reaching its minimum at the outer silver surface, in spite of the fact that the transition temperature remains high, and excluding the spatial variation which will occur in the solution of integral equations.

The ideas discussed here have many experimental consequences. It would be of great interest to measure the critical temperature as a function of film thickness when specimens have been placed on one another in a high vacuum to reduce the surface layer. The influence of different effective masses and Fermi momenta in the two neighboring specimens as well as of the purity of the nonsuperconducting film on T_c is of interest. Also the variation of T_c with surface layer would be interesting, especially in the light of recent tunneling experiments. More detailed theoretical investigations of these and related questions are being pursued at present.

The author wishes to thank Drs. Smith, Shapiro, Miles and Nicol for communication of their results prior to publication. He also wishes to thank Professor J. Dillon for a very helpful conversation.

References

1. S. Shapiro, P. H. Smith, J. L. Miles and J. Nicol, *Phys. Rev. Letters* **6**, 686 (1961).
2. H. Meissner, *Phys. Rev.* **117**, 672 (1960) (See for further references).
3. R. H. Parmenter, *Phys. Rev.* **118**, 1173 (1960).
4. J. Bardeen, L. N. Cooper and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).
5. D. Pines, *Phys. Rev.* **109**, 280 (1958).
6. L. P. Gor'kov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **34**, 735 (1958) [*Soviet Phys.—JETP* **7**, 505 (1957)]. P. C. Martin and J. Schwinger *Phys. Rev.* **115**, 1342 (1959). L. P. Kadanoff and P. C. Martin (to be published).

Received June 15, 1961